

CONTRIBUTIONS FROM THE LABORATORY OF THE UNIVERSITY OF PENNSYLVANIA.

No. XIV.

I. A new Monochlordinitrophenol and an Aniline derivative of α -Monochlordinitrophenol. II. Beryllium Borate.

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When fuming nitric acid is allowed to act upon pure monochlorosalicylic acid, there is produced not only the corresponding monochloronitrosalicylic acid (in small quantities), but the nitration usually extends so far as to cause the carboxyl group to disappear, and two nitro-groups enter, leaving us a monochlordinitrophenol. The formation of this latter compound was first effected in this manner by Rogers (Inaugural Dissertation, Göttingen, 1875). The phenol showed a constant fusing point of 79° - 80° C., was rather insoluble in cold water, more readily soluble in warm, and crystallized from its aqueous solutions in long yellow needles.

The salts of this acid are very beautiful, but it will suffice for our purpose to mention only the potassium derivative, which separates from its solutions in long, beautiful silky-red needles, without any water of crystallization.

The above phenol and its potassium salt I also produced, but, after working with the latter for some time, I suspected the presence of another compound, and by repeated re-crystallization from aqueous solutions I finally obtained not only the red potassium salt, but a similar compound which separated in large bundles consisting of orange-colored needles. These, after being completely separated from the red salt, were subjected to an analysis to ascertain their constitution.

Analysis of the red colored salt.

.1691 grms. salt, dried at 130° C., were placed in a platinum crucible, a few drops of conc. sulphuric acid added, and a gentle heat applied. The K_2SO_4 that remained = .0264 grms., which corresponded to 15.60% potassium. The salt is anhydrous. The calculated percentage of K in $C_6H_2Cl(NO_2)_2OK$ is 15.23%. There was, therefore, no doubt as to the constitution of this salt.

MONOCHLORDINITROPHENOL.

Fusing point 80° C.

The free acid crystallized from aqueous solutions in long yellow needles, which fused at 80° C and solidified again at 69° C. It is also identical with the phenol of Rogers (see above) and the α -Chlordinitrophenol of Faust and Saane (Annalen der Chemie u. Pharmacie, 1870. 7 Supplementband. 2 Heft S. 174).

Analysis of the yellow colored salt.

Water Determination.—1617 grms. air dried salt lost upon heating at 140° for four hours .0168 grms. $H_2O = 10.39\%$. $1\frac{1}{2}$ mols H_2O require 9.53% .

Potassium Determination.—1449 grms. substance gave, upon evaporation with sulphuric acid, .0480 grms. $K_2SO_4 = 14.86\%$ potassium. From this we see that this salt is also a derivative of a monochlordinitrophenol. The formula is $C_6H_2Cl(NO_2)_2OK + 1\frac{1}{2}H_2O$.

This salt is much more soluble than the red compound. The color of the latter is so intense as to entirely obscure the yellow, which consequently is overlooked unless great care is exercised in re-crystallizing the red compound.

MONOCHLORDINITROPHENOL.

Fusing point 79° – $80^{\circ}C$.

Upon mixing a cold solution of the yellow salt with dilute nitric acid the corresponding phenol separated in yellowish colored masses, which upon being washed and re-crystallized several times from aqueous solutions, separated in rather long lemon-yellow colored needles. The fusing point of this compound remained constant at 79° – $80^{\circ}C$. The point of solidification was $25^{\circ}C$., considerably lower than that of the acid corresponding to the red needles. In cold water the acid is rather insoluble, readily dissolved on heating.

Another difference noticed between the free acid from the red silky needles, and that just above described is in the silver salts. The former yields a soluble salt crystallizing in long bright red colored needles, the latter one separates out in bronze colored needles which possess a marked metallic lustre.

This new Chlordinitrophenol is usually formed in very small quantities, therefore I have not been able to subject it to as thorough an investigation as I desired. The material with which I worked was, however, perfectly pure, and as I have obtained the compound at various times, and the analytical results being the same on all occasions, I do not hesitate to announce the above acid as another of the many possible compounds having this composition. In regard to the position of the (NO_2) groups I cannot as yet give any definite information.

a-MONOCHLORDINITROPHENOL-ANILINE.

A small quantity of a-Chlordinitrophenol was mixed with sufficient aniline to dissolve the former in the cold. As soon as the two compounds were brought in contact the solution assumed a beautiful red color, which imparts to the skin a rather difficultly removable yellow stain. The solution was gently warmed on a water bath for ten minutes, and the liquid then poured from the flask containing it into a rather large watch glass and allowed to cool. Upon cooling there separated hard nodular crystals, which were pressed well between paper and dried by exposure to the air,

then dissolved in warm water, from which, on cooling, long curled light-yellow needles separated. The fusing point of this compound after repeated re-crystallizations remained constant at 137°C . When solutions of the compound in water are boiled hard aniline separates out. An analysis of the substance indicated it to be a union of one mol. chlordinitrophenol with a like amount of aniline— $\text{C}_6\text{H}_2\text{Cl}(\text{NO}_2)_2\text{CH}.\text{C}_6\text{H}_5\text{NH}_2$.

Analysis.—1.221 grms dried substance burned with lead chromate gave .0188 grms. Carbon = 46.19% C. The hydrogen determination was lost. The theoretical percentage of carbon demanded by the above compound is 46.22% C.

With the ammonia-cobalt bases of Genth and Gibbs, a-Monochlordinitrophenol yields exceedingly beautiful compounds. My results in this direction will be given later.

BERYLLIUM BORATE.

Some time ago I was working with beryllium and added to a solution of its chloride an excess of a rather concentrated borax solution. An immediate precipitation was the result. The precipitate was thrown upon a filter and washed with hot water, until a drop of the washings evaporated upon platinum foil left no residue.

The precipitate was dried and tested for boracic acid, but this was not found present. Another portion of the same precipitate subjected to an analysis proved it to be nothing more than beryllium hydrate, consequently if the borate had been at first produced, the subsequent boiling with hot water had decomposed it.

Another portion of the beryllium chloride was treated in a similar manner. The precipitate was brought on the filter to allow the liquid to drain off, and then rinsed with cold water into a small flask, water added, and allowed to stand for some time—being occasionally shaken. The precipitate was then brought on to a filter and dried by exposure to the air.

Boracic acid was found present when the tests were made.

Analysis gave me the following percentages of beryllium oxide: 6.98 BeO and 6.89% BeO.

The boracic acid was not estimated.

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